



Quantitative analysis on the adsorbed amount and structural characteristics of spin self-assembled multilayer films

Jinhan Cho^a, Seung-Heon Lee^a, Huiman Kang^a, Kookheon Char^{a,*}, Japil Koo^b, Byoung Hoon Seung^b, Ki-Bong Lee^b

^a*School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-744, South Korea*

^b*Department of Physics, Pohang University of Science and Technology, San 31, Hyoja-dong, Nam-gu, Pohang 790-784, Kyungbuk, South Korea*

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Abstract

In this study, we demonstrate that the adsorbed amount of respective layers in spin self-assembled multilayer films can be controlled and predictable using an empirical power-law equation in terms of spin speed and initial solution concentration. The amount of a pair of polyelectrolytes deposited per bilayer rapidly increases with increasing polyelectrolyte concentration up to 12.5 mM while the solution concentration above 16 mM has no appreciable effect on the adsorbed amount. The adsorbed film thickness per bilayer is shown to be easily controlled from about 5 to 40 Å and proportional to constant power exponents of -0.34 and 0.78 with respect to the spinning speed (Ω) and the mole concentration of polyelectrolytes, respectively. We also demonstrate with synchrotron X-ray reflectivity measurement that the alternating organic/inorganic ultrathin films fabricated by the spin self-assembly process contain highly ordered internal structure and retain unique optical characteristics determined by the boundary condition at both the substrate/multilayer film interface as well as the multilayer/air interface.

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1. Introduction

In recent years, there has been considerable interest in ultrathin multilayer films using layer-by-layer self-assembly (SA) method because of their wide applications such as sensors, integrated optics, coatings for friction reduction, biological surface, colloidal particles, light-emitting devices, or surface orientation layers [1–14]. First introduced by Decher in 1991, it has been demonstrated by many research groups that the adsorbed amount of polyelectrolytes, surface morphology, internal structure of multilayer films and physical or chemical structure of adsorbed polyelectrolytes are strongly influenced by several variables such as the pH, the concentration and the ionic salt amount of polyelectrolyte solution [15–24]. Furthermore, this layer-by-layer SA method has been extended to the SA based on the spin coating for both improved internal structure and film preparation efficiency [25–29].

Recently, we have reported the spin SA method as a modified layer-by-layer method to prepare stratified multilayer films by varying solution concentration and spin speed [25]. In our previous paper, the differences in the adsorption of polyelectrolytes between the dip and the spin SA method were presented and it was demonstrated that highly ordered multilayer films could be easily prepared by the spin SA method [25]. A few years ago, Hong et al. have reported that the use of horizontal spinning after each dipping as a drying step induces more dense and compact films [26]. Also, Dubas and Schlenoff have shown that multilayer films composed of PSS and PDADMAC can be prepared by immersing a spinning substrate in polyelectrolyte solutions [27]. However, to the best of our knowledge, these methods have mainly been based on the adsorption steps used in the dipping method and also put little emphasis on both the experimental variables (spin speed and polyelectrolyte concentration) and the adsorption mechanism applied between a polyelectrolyte layer and a sublayer during the high-speed spinning. An independent study performed by

* Corresponding author. Tel.: +82-2-880-7431; fax: +82-2-888-7295.
E-mail address: khchar@plaza.snu.ac.kr (K. Char).

Chiarelli et al. has recently reported a slightly different version of the spin assembly method using soft heating after the film deposition and has also demonstrated the application of the spin assembly to a variety of polyelectrolytes [28,29].

In the present study, we describe the quantitative analysis on the relationship between the adsorbed amount of polyelectrolytes deposited by the spin SA method and the spin speed as well as the polyelectrolyte concentration. Although our analysis is based on an empirical equation, we believe that this is the first step toward the better understanding of the mechanism of multilayer formation prepared by the spin SA. In addition, we investigate the internal ordering of individual layers in multilayer films fabricated by the spin SA using the synchrotron X-ray reflectivity data and demonstrate the effect of electron density difference at the interfaces due to the change of deposition sequence on the reflectivity spectra.

2. Experimental

Materials. Poly(sodium 4-styrenesulfonate) (PSS) (Aldrich, $M_w = 70,000$) and poly(allylamine hydrochloride) (PAH) (Aldrich, $M_n = 50,000$ – $65,000$) were used as an anionic and a cationic polymer, respectively. All the aqueous polyelectrolyte solutions were used without pH adjustment and the addition of ionic salt in present study. CdS nanoparticles carrying amine ($-\text{NH}_3^+$) groups onto the surfaces were used for the preparation of organic/inorganic multilayer films. This nanoparticle solution was obtained by treating cadmium acetate dihydrate with thioacetamide in the presence of 2-mercaptoethylamine hydrochloride [30].

Build-up of spin SA multilayer films. Negatively charged quartz substrates for the deposition of positively charged PAH or CdS– NH_3^+ nanoparticles were initially cleaned by ultrasonification in a hot mixture of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7/3) for 3 h. They were then heated in a mixture of $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$ (5/1/1) at 80°C for 1 h, and subsequently dried by N_2 gas purging. For the spin SA multilayer films, a few drops of positively charged PAH or CdS– NH_3^+ solution were slowly placed on the edge of a substrate of $2\text{ cm} \times 2\text{ cm}$ (the position of solution dropping relative to the substrate was maintained as close as possible) and the solution was then completely covered on the total area of the substrate in short time with high wettability. This procedure can produce a uniform film on a large area except the edge of the substrate. After the solution deposition, the substrate was rotated with a spinner at a fixed rotating speed (typically, 4000 rpm) up to the point where the substrate was enough dried and then the substrate was thoroughly rinsed twice with a plenty of deionized water with a spinner in the same condition as the adsorbate deposition [25]. Negatively charged PSS layer was also sequentially deposited onto the substrate using the same procedure as mentioned above.

3. Results and discussion

3.1. Quantitative analysis on the adsorbed amount

In order to investigate the adsorption of polyelectrolyte chains assisted by the viscous and electrostatic forces during the spinning process, we obtained the dependence of the mole concentration of polyelectrolyte solutions on the adsorbed amount as a function of the number of (PAH/PSS) bilayers, as shown in Fig. 1(a). The spinning condition for each layer deposition was fixed at 4000 rpm for 15 s. As indicated by the slopes of almost linear lines, the amount of polyelectrolytes deposited per bilayer rapidly increases with increasing the polyelectrolyte concentration up to 12.5 mM. Fig. 1(b) quantitatively shows both the adsorbed amount and the thickness per bilayer with increasing the mole concentration of polyelectrolytes. The resulting film thickness per bilayer increases from 5 to 40 \AA . We also found that the solution concentration above 16 mM has no appreciable effect on the adsorbed amount. This observation

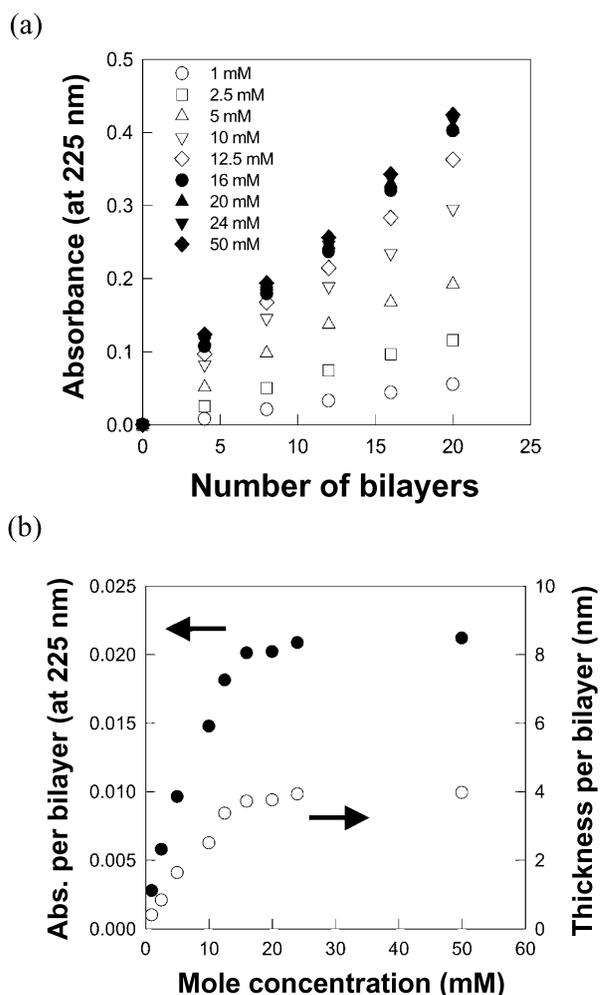


Fig. 1. (a) The increase of absorbance of $(\text{PAH/PSS})_n$ as a function of bilayer number. (b) The effect of mole concentration on both the adsorbed amount (\bullet) and the thickness per PAH/PSS bilayer (\circ) prepared by spin SA method. Spinning speed is fixed at 4000 rpm.

suggests that it is possible to precisely control the adsorbed amount of polyelectrolytes in multilayer films by simply changing a wide range of solution concentration in spite of the strong repulsion among polyelectrolyte chains with the same charge. Although the increase of solution concentration tends to produce a thicker adsorbed polymer layer due to the adsorption driving forces such as viscous and electrostatic forces, the excess adsorbed layer with weak binding sites are readily eliminated by the desorption driving forces such as centrifugal and air shear forces.

When the spin speed is increased at a fixed solution concentration, the extent of desorption of weakly bound chains can also be quantitatively measured. Fig. 2(a) represents a log–log plot of the average absorbance per bilayer as a function of spinning speed for several polyelectrolyte concentrations. We found that the absorbance, linearly proportional to the film thickness, decreases with the spinning speed with a scaling exponent of 0.34. The

absorbance per bilayer as a function of initial polyelectrolyte concentration is also shown in Fig. 2(b). With the spin speeds tested in present study, the absorbance per bilayer increases with polyelectrolyte concentration with a scaling exponent of 0.74 up to a limiting concentration of about 10 mM above which the absorbance per bilayer levels off. The resulting absorbance is related to the spinning speed Ω and the initial concentration C_i as follows:

$$A(\propto H) \sim \Omega^{-\alpha} C_i^{\beta}, \text{ with } \alpha \approx 0.34 \text{ and } \beta \approx 0.74$$

where A is the absorbance per bilayer and H is the bilayer thickness. On the other hand, many theoretical models and experimental results based on the spin coating of single layer films of thickness ranging from micrometer (μm) to millimeter (mm) have shown that the film thickness H is, with reproducibility, proportional to the -0.5 power of the spinning speed and the 1.50 – 2.47 power with respect to the initial polymer concentration [31–33]. These differences in the power exponents with respect to both the spinning speed and the initial solute concentration obtained for the ultrathin multilayer films could be explained, though not fully understood, by the strong interaction such as the electrostatic force between a sublayer (or a substrate) and a coating layer and the facile elimination of weakly adsorbed polyelectrolyte chains. As the thickness of a film layer is increasingly smaller, the interaction effect between a sublayer and a coated overlayer becomes more important and therefore significantly reduces the elimination rate of adsorbed layer caused by desorption forces. Conversely, since the weakly bound layers, which increase with increasing polyelectrolyte concentration, are thoroughly eliminated during the washing step, we believe that the value of power exponent β depending on the polyelectrolyte concentration should be smaller in the case of ultrathin films than that given for relatively thick single layer films. As a result, considering this relation between adsorbed amounts of polyelectrolytes and spin speed as well as initial solution concentration, the respective layer thickness in a multilayer film can be exactly controlled and easily predicted.

3.2. Structural characteristics of multilayer ultrathin films

We have previously reported the internal structure of highly ordered spin SA multilayer films (i.e., $\text{Si}/[(\text{PAH}/\text{PSS})_n/(\text{PAH}/\text{anionic CdS})_1]_m/\text{Air}$, $[n+1]m = 20$ or 21) exploiting the significant electron density difference between the PAH polyelectrolyte layer and the anionic CdS nanoparticle layer [25]. In this case, it should be noted from the X-ray reflectivity experiment that these m -periodic spin SA multilayer films distinctly exhibit $(m-1)$ oscillations of the Kiessig fringes, contrary to the $(m-2)$ oscillations predicted by the grating theory, between the adjacent Bragg reflection peaks [34].

For better understanding of the X-ray reflectivity results obtained with the well-ordered internal structure, we also

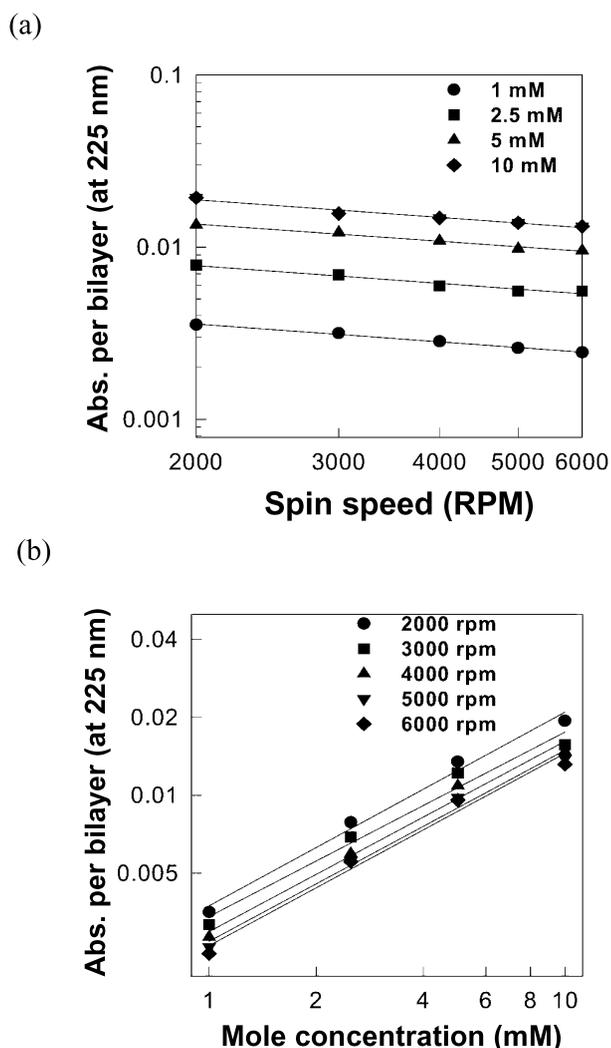


Fig. 2. The effect of spinning speed (a) and mole concentration of polyelectrolytes (b) ranging from 1 to 10 mM on the adsorbed amount of PAH/PSS bilayers prepared by the spin SA method. Each point in the figure represents the average absorbance per bilayer for up to 20 bilayers.

prepared the spin SA organic/inorganic multilayer films using positively charged CdS nanoparticles (i.e., Si/[(cationic CdS/PSS)₁/(PAH/PSS)_n]_m/Air, $[n + 1]m = 20$ or 21), as shown in Fig. 3(a), instead of negatively charged CdS (see Figure 4 in Ref. [5]). In this case, the (cationic CdS/PSS) bilayer thickness of 30 Å is slightly higher than the (PAH/anionic CdS) bilayer thickness of 26 Å since the average diameter of cationic CdS nanoparticles is about 21 Å and the thickness of PSS polyelectrolyte layer adsorbed onto CdS is about 9 Å. The increase in *d*-spacing due to the insertion of an organic (PAH/PSS) bilayer

between the (cationic CdS/PSS) bilayers is, within experimental uncertainty, consistent with the (PAH/PSS) bilayer thickness of 24 Å as previously reported [25].

The multilayer films composed of cationic CdS nanoparticles and polyelectrolytes, in comparison with the spin self-assembled (polyelectrolytes/anionic CdS) multilayer films with an internal structure as depicted in a schematic of Fig. 3(b), have different electron density boundary conditions at the interfaces between a Si substrate and the bottom of a multilayer film as well as between the top of a multilayer film and air since inorganic CdS nanoparticles

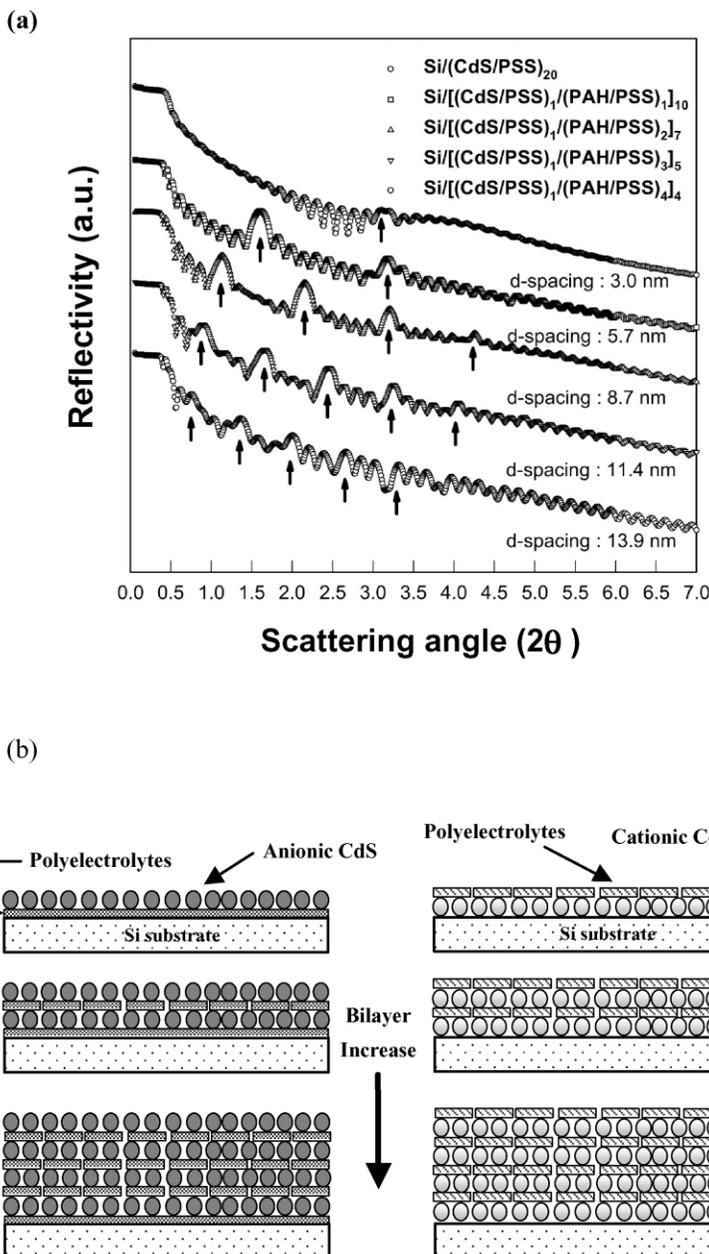


Fig. 3. (a) X-ray reflectivity curves of [(cationic CdS/PSS)₁/(PAH/PSS)_n]_m ($[n + 1]m = 20$ or 21) films prepared by the spin SA method. The increase of the number of organic (PAH/PSS) bilayer from 0 to 4 causes the increase in *d*-spacing between the organic and the inorganic nanoparticle layers ranging from 3.0 to 13.9 nm. The arrow symbols in the figure indicate the Bragg peaks of such internal structure. (b) Schematic of the internal structure of spin SA (polyelectrolytes/anionic CdS)_n (X-ray reflectivity data given in Ref. [5]) and spin SA (cationic CdS/polyelectrolytes)_n multilayer films based on different electron densities at the interfaces due to different deposition process.

having the relatively high electron density were used as the first layer right on top of the Si substrate and organic polyelectrolytes having relatively low electron density as the top layer. It should be here noted that the electron densities of CdS nanoparticles, organic polyelectrolytes, and Si substrate, which are taken from literatures [35,36], are 1.299 [37], 0.40, and $0.68 \text{ e}/\text{\AA}^3$, respectively. In this case, the number of small oscillations between the adjacent Bragg peaks was found to be $(m - 2)$, fully consistent with the prediction of the grating theory: 18 oscillations for the (cationic CdS/PSS)₂₀, 8 oscillations for the [(cationic CdS/PSS)₁/(PAH/PSS)₁]₁₀, 5 oscillations for the [(CdS/PSS)₁/(PAH/PSS)₂]₇, 3 oscillations for the [(cationic CdS/PSS)₁/(PAH/PSS)₃]₅, and 2 oscillations for the [(cationic CdS/PSS)₁/(PAH/PSS)₅]₄ films (see Fig. 3(a)). Although we would not make a quantitative analysis of the X-ray reflectivity results in this study, it is strongly believed that the variation of boundary conditions at the interfaces of substrate/film and film/air plays an important role in optical characteristics of the multilayer films and that the subtle difference between the X-ray reflectivity results, induced by the change of boundary conditions as shown in Fig. 3(b), can only be observed with multilayer films with high internal order and sharp interfaces between adjacent layers.

4. Conclusion

We have demonstrated that the adsorbed amount of polyelectrolytes determined by adsorption and desorption forces during the spin SA process can be described by a power-law function in terms of spinning speed and initial polymer concentration. It should also be noted that the respective layer thickness of the ultrathin multilayer films could be exactly controlled and easily predicted using the power-law function.

In addition, it is demonstrated from the synchrotron X-ray reflectivity measurement of multilayer ultrathin films that the internal structure of the multilayer thin films is highly ordered and the change of boundary conditions of electron density at interfaces of substrate/films and films/air has a significant effect on the optical characteristics of multilayer films. We believe that the present study on the boundary conditions of organic/inorganic multilayer films can stimulate the systematic investigation of experimental variables related to the nanostructure of organic/inorganic films and, eventually, of correlating the film's internal structure to its optical property.

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- [37] The mass and density of CdS carrying 64 electrons are estimated to be $237.75 \times 10^{-24} \text{ g}$ and $4.826 \times 10^{-24} \text{ g}/\text{\AA}^3$, respectively. As a result, the electron density of CdS carrying 64 electrons is calculated to be $1.299 \text{ e}/\text{\AA}^3$.